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DIRECT EVIDENCE FOR α,α -DIFLUOROCARBOCATIONS IN THE REACTIONS OF CHLOROACETIC ACIDS WITH SULPHUR TETRAFLUORIDE

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SUMMARY

Reactions of chloro-, and dichloroacetic acids with sulphur tetrafluoride and p-xylene or mesitylene gave, besides chlorofluoroethanes $\text{CF}_3\text{CH}_2\text{Cl}$ and CF_3CHCl_2 , small yields of chlorofluoroethylarenes $\text{ArCF}_2\text{CH}_2\text{Cl}$ and $\text{ArCF}_2\text{CHCl}_2$, and chloroacetylarenes ArCOCH_2Cl and ArCOCHCl_2 (Ar=p-xylyl or mesityl). With mesitylene, compounds $\text{ArCF}_2\text{CH}_2\text{Cl}$ and $\text{ArCF}_2\text{CHCl}_2$ are formed exclusively by alkylation of mesitylene with carbocations $\text{CH}_2\text{ClCF}_2^+$ and $\text{CHCl}_2\text{CF}_2^+$, respectively, while with p-xylene, both, alkylation and the consecutive fluorination of chloroacetyl-p-xylenes with SF_4 can contribute to the formation of the corresponding chlorofluoroethyl-p-xylenes.

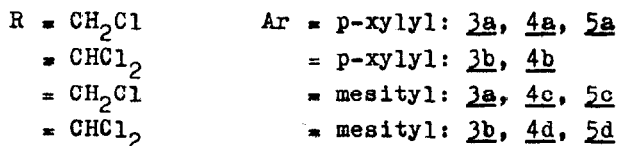
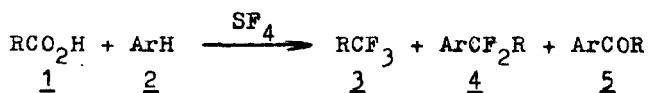
INTRODUCTION

Reactions of carboxylic acids with sulphur tetrafluoride have been systematically studied in this Laboratory [1]. On the basis of numerous results a mechanism involving fluoro-carbonium ions of the type RCF_2^+ has been proposed for these reactions [1d] but no direct evidence for such intermediates was so far reported. In an attempt to trap these intermediates and therefore to verify the proposed mechanism, reactions of

chloro- and dichloroacetic acids with sulphur tetrafluoride in the presence of arenes i. e. p-xylene and mesitylene as trapping agents were conducted.

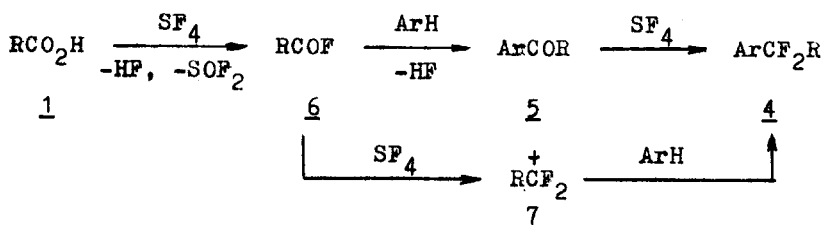
RESULTS AND DISCUSSION

Reactions of chloroacetic acids 1 with arenes 2 and sulphur tetrafluoride gave, in general, three types of products: chlorofluoroethanes 3, chlorofluoroethylarenes 4 and chloroacetylarenes 5.



1-Chloro-2,2,2-trifluoroethane 3a and 1,1-dichloro-2,2,2-trifluoroethane 3b were formed as the main products in the reactions with chloro- and dichloroacetic acids, respectively. Gem-difluoroethylarenes 4 were obtained from all investigated reactions. The yields of 4 varied from 3% to 27%, depending on the nature of the reactant acid and arene. Chloroacetylarenes 5 were formed with yields up to 13.2% (Table 1).

Ketones 5 are the result of acetylation of the arenes with chloroacetylfluorides 6, which are readily formed in the first stage of the reaction of chloroacetic acids with sulphur tetrafluoride. Two ways to obtain gem-difluoroethylarenes 4 may be considered: a consecutive reaction of ketones 5 with sulphur tetrafluoride, and a direct alkylation of the arenes by fluorocarocations 7, which were postulated as intermediates in the reaction of acid fluorides with sulphur tetrafluoride leading to trifluoromethyl compounds and $\alpha, \alpha, \alpha', \alpha'$ -tetrafluoroethers [1].



It has been found that chloroacetylxlene 5a synthesised by another method reacted with sulphur tetrafluoride to give the corresponding gem-difluoroethyl-p-xylene 4a, and so both possible pathways may contribute to the formation of the latter compound. However, chloroacetylmesitylene 5c and 5d, in agreement with previous findings [2], failed to react further with sulphur tetrafluoride, so gem-difluoroethylmesitylenes 4c and 4d must be formed exclusively via fluoroalkylation of mesitylene with $\text{CH}_2\text{ClCF}_2^+$ and $\text{CHCl}_2\text{CF}_2^+$ cations.

EXPERIMENTAL

Boiling and melting points are uncorrected. NMR spectra were taken on a JEOL JNM-4H-100 spectrometer: chemical shifts are in p.p.m. from internal CCl_3F for ^{19}F spectra (positive upfield) and from internal TMS for ^1H spectra (positive downfield). GLC analyses were performed with a Chromatron GCHF 18.3.4 instrument using a 3.5m x 4mm column packed with Chromosorb G coated with 3% silicone oil SE-52. Sulphur tetrafluoride was prepared by a standard technique used in this Laboratory [1a]. The chloroacetic acids and the arenes used were commercial pure-grade products.

Reactions of chloroacetic acids 1 with SF_4 and arenes 2

The reactions were carried out in a 0.1dm³ stainless steel autoclave: 0.19 mole of the acid and 0.2 mole of the arene were placed in the autoclave, cooled in dry ice-acetone mixture, evacuated to 1-2 mmHg, and then 0.3 mole of SF_4 was liquified

TABLE 1

Analytical and characteristic data of α, α' -difluoroethylarenes 4 and chloroacetylarenes 5

S. No.	Yield ^a %	B.p. (°C/mmHg) or m.p. (°C)	¹ H and ¹⁹ F ^c NMR (in CCl ₄)		Analyses (%)			
			(CH ₂ Cl) or (CHCl ₂)	(CF ₂) J (HF)	Found	Calculated	C	H
4a	3.0	76-78/2	3.9	98.9	12.5	58.7(58.7)	5.4(5.4)	18.8(18.6)
4b	27.0	140-142/30	5.9	101.8	8.9	50.0(50.2)	4.2(4.2)	15.8(15.9)
4c	5.8	36-37	3.8	92.6	12.5	60.6(60.4)	6.1(6.0)	17.3(17.4)
4d	6.5	87-90/2	6.1	95.6	8.8	52.3(52.2)	4.8(4.8)	15.3(15.0)
5a	6.8	30-31 ^d	4.4			65.7(65.8)	6.0(6.1)	
5c	13.2	68-69 ^e	4.4			67.3(67.2)	6.7(6.7)	
5d	12.0	71-72	6.2			57.3(57.2)	5.3(5.2)	

a) Mole percent of the acid.

b) The signals of compounds 4a-4d appeared as triplets and of compounds 5a-5d as singlets.

c) The signals of compounds 4a-4d appeared as triplets or doublets with further splitting due to the through space coupling with the CH₃ groups on the arene ring.

d) Lit. 32° [3]. e) Lit. 67-69.5° [4].

in it. The charged autoclave was heated in a rocking muffle furnace for 3 hours at 80-90° for the reactions with p-xylene, and at 50-60° for the reactions with mesitylene. After the reaction had run to completion, the autoclave was allowed to cool and gaseous products i.e. haloethanes 3, SOF₂, and HF were let out. The residue was poured on iced water, organic layer was washed with water, dried over MgSO₄ and distilled. Mixtures of compounds 4a and 5a, 4c and 5c, and 4d and 5d were subjected to separation by column chromatography on Al₂O₃ (Woelm II activity) using petroleum ether (b.p. 60-80°) as the eluent.

Reactions of chloroacetylarenes 5a and 5c with SF₄

1-Chloroacetyl-2,5-dimethylbenzene 5a (1.8 g, 0.01 mole), SF₄ (6.0 g, 0.05 mole), and two drops of anhydrous hydrogen fluoride were placed in a 0.03 dcm³ stainless steel autoclave and heated at 80-90° for 3 hours. The reaction mixture was treated as above and distilled to give 1.7 g (yield 82%) of 1-(β-chloro-α,α-difluoroethyl)-2,5-dimethylbenzene 4a.

A similar reaction with 1-chloroacetyl-2,4,6-trimethylbenzene 5c gave only the unreacted substrate.

ACKNOWLEDGEMENT

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REFERENCES

- 1 W. Dmowski and R. Koliński, Pol.J.Chem., a) 47 (1973) 1211; b) 48 (1974) 1697; c) 52 (1978) 71; d) 52 (1978) 547.
- 2 C. Kullgren, Of. Sv., (1896) 389.
- 3 F. Kunckell, Ber., 30 (1897) 579.
- 4 H.R. Snyder and R.W. Roeske, J. Amer. Chem. Soc., 74 (1952) 5820.